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The statistical modeling of the platinum nanoparticles in the transition area from the five-fold symmetry structure to the crystal lattice

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Abstract

This paper deals with the atom energy mean value of the platinum nanoparticles of various size (from 300 to 3000 atoms that approximately corresponds to the transition threshold from the icosahedral structure to the face-centered cubic one) on the face-centered cubic lattice and on the five-fold symmetry one, with the application of the modified Metropolis algorithm based on the Monte-Carlo method. When calculating the energy the quantum Sutton-Chen potential is used.

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Keywords: Metropolis algorithm; platinum nanoparticles; quantum Sutton-Chen potentials

1. Introduction

The calculation of the equilibrium structure and metal nanoparticles shape is necessary for their properties prediction. It is known from the experiments that an icosahedrons, a decahedron, a cubooctahedron and also their truncated modifications are the typical nanoparticles shapes. The Wulff construction predicts that the five-fold symmetry shapes (an icosahedron or a decahedron) are more stable for the small sized nanoparticles and the cuboctahedral nanoparticles having a face-centered crystal lattice are more energetically favorable for the large ones. Searching for the global energy minimum of nanoparticles is a computationally expensive task. In the Cambridge Cluster Database [1] there are optimized nanoparticles configurations of approximately 300 atoms calculated using many-body potentials [2]. It should be noted that typically only putative global minima are found

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without any proof that they are really global. Taking into account the recently published data in this field [3, 4], the feasible size of nanoparticles today is limited at least by 1.000 atoms. The Ino's model predicts the transition threshold to be approximately 10 nm [5], while the calculations based on the quantum Sutton-Chen potential does 2 nm [6], these models give a possible transition threshold in the range approximately from 250 to 10000 atoms. Therefore to analyze the transition which will be carried out in the atomic-scale model, it is necessary to make some assumptions of the structure of the expected equilibrium configuration. Nowadays there is a large number of studies carried out in this field using various methods of molecular dynamics and different potentials [7, 8]. Recently the comparative study of local energy minima for the various motives in the putative transition area from the five-fold symmetry to the face-centered cubic lattice was conducted for a number of transition metals in a wide size range [9]. As part of the study it was shown that at least for the nanoparticles having the ideal shape (from the magic number of atoms), the energy differences of varied motives and the energy itself are well approximated by the logarithmic functions of the nanoparticles size. This result allows to define the size range of the stability of nanoparticles of various shapes with minimum efforts. The objective of this research is the equilibrium shape of the platinum nanoparticles of nonideal shape (with incomplete external atom shell) finding in the range from 300 to 3000 atoms, the empirical dependency of the one atom mean energy on the number of atoms representing, the comparison of the obtained dependency with the results presented in the paper [9].

2. Study subject

In this study the dependency verification of one atom energy on the size was carried out for the nanoparticles of nonideal shapes with incomplete external atomic shells, with the steps and adatoms on the surfaces. The verification was realized for the Pt nanoparticles in the transition area from the five-fold symmetry structure to the crystal one (from 300 to 3000 atoms according to the obtained data [9]).

3. Methods

The modeling was performed within the lattice model on the face-centered cubic lattice and on the non-crystalline lattice with five-fold symmetry. The cut-off radius was limited by the 5th coordination sphere, the relaxation was previously carried out on the lattices to make the ideal lattices more realistic. The quantum non-additive empirical Sutton-Chen potential was used for the calculations [10]:

$$E = \varepsilon\left[\frac{1}{2}\sum_{i\neq j}\sum V(r_{ij}) - c\sum_i \sqrt{p_i}\right],\ V(r) = (a/r)^n,\quad p_i = \sum_{i\neq j}\left(\frac{a}{r_{ij}}\right)^m \tag{1}$$

with the parameters $a = 3.9163,\ \varepsilon = 9.7894\cdot 10^{-3},\ c = 71.336,\ m = 7,\ n = 11$.

The potential parameters were calculated in the paper [11] on the basis of the requirement so the optimum parameters can correspond to the obtained experimentally cohesive energy of platinum and considering the lattice a length parameter. In order to consider the quantum effects, the energy at the absolute zero was included into the calculations. The potential parameters were optimized to describe lattice a parameter, cohesive energy, bulk modulus, elastic constants, phonon dispersion, vacancy formation energy and surface energy. The optimization was performed with poorer accuracy for elastic constants but with better accuracy for surface energy. The applying of this potential is determined by the fact that the particle equilibrium shape is specifically defined by the surface energy.

In order to calculate the nanoparticles equilibrium shape, the Monte-Carlo method was used. In order to accelerate the convergence of algorithm, the vacancies and atoms lists were used on the nanoparticle surface with account of the appropriate corrections of trial steps acceptance probability, the details of the applied algorithm are described in the paper [12]. Furthermore to accelerate the convergence and since it is possible to ignore the detailed balance condition to obtain the particle shape with the minimum energy, the energy of atoms which can be considered to lie on the surface was limited and consequently the above mentioned atoms can become the vacancies.

4. Results and discussion

The energy E quickly reached the minimum and formed a stable plateau when modeling. This tells about the algorithm sufficient efficiency and suggests that the global energy minimum or the value close to it was reached.

As a result of modeling by the Monte-Carlo method the equilibrium nanoparticles configurations between 300 and 3000 atoms in size with 80 atoms step were obtained. The obtained mean energy values of the platinum nanoparticle atom decrease monotonously that corresponds to the theoretical predictions. In case of the face-centered cubic lattice the equilibrium configurations are of the truncated octahedron shape and in case of the five-fold structure - the shape close to the ideal icosahedron (as shown in Fig. 1 and 2). But since the atoms amount does not correspond to the magic numbers, vacancies, adatoms and steps appear on the surface.

By the paper [9] data and according to the obtained data for the arbitrary number of atoms, the mean energy dependencies per atom on the number of atoms were offered which are approximated by the following functions $y = c + (a + x)/(b - x / 5.84)$, the constant 5.84 is equal to the value of cohesive energy for platinum while parameter c characterizes the asymptote deviation from cohesive energy. One can see the offered dependencies and their approximation for the arbitrary number of atoms in Fig. 3. The approximations for the nanoparticles consisting of the magic number of atoms and of the arbitrary ones are presented in Fig. 4. The approximation coefficient is more than 0.996 in case of the magic numbers while in case of the arbitrary number of atoms it is more than 0.998. The approximating functions parameters are specified in Table 1. For the given approximating functions at $x \to +\infty$, the asymptotes exist $y = -5.713$, $y = -5.719$ (for the magic number of atoms), $y = -5.729$, $y = -5.724$ (for the arbitrary number of atoms), the given values are close to the experimental cohesive energy values for platinum - 5.84.

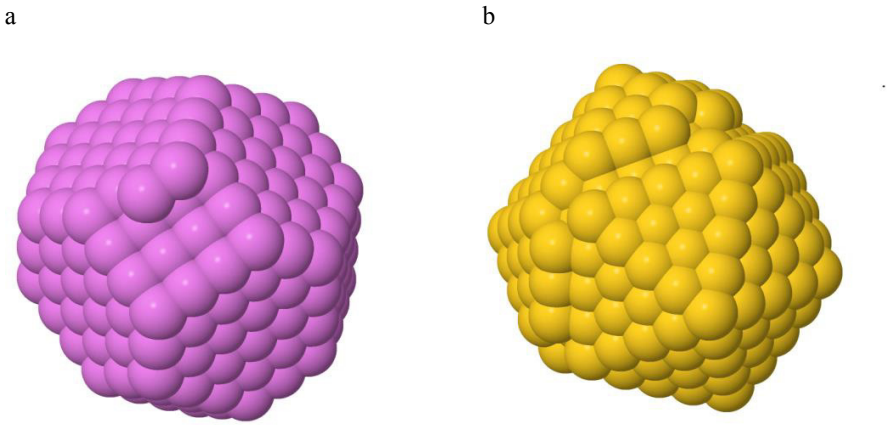

Fig. 1. The examples of the computed platinum nanoparticles for 380 atoms, (a) – FCC lattice, (b) – the five-fold symmetry lattice.

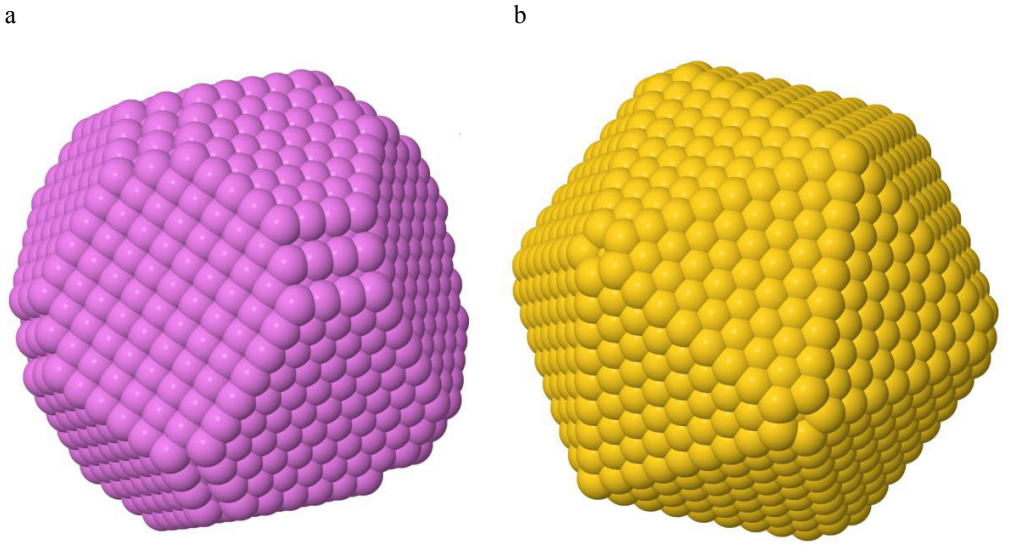

Fig. 2. The examples of the computed platinum nanoparticles for 2860 atoms, (a) – FCC lattice, (b) – the five-fold symmetry lattice.

Table 1. The approximating functions parameters.

		Nanoparticles from the magic number of atoms	Nanoparticles from the arbitrary number of atoms
Face-centered cubic structure (FCC structure)	a	250.93381	407.61321
	b	-47.9741	-76.23547
	c	0.12711	0.11063
Five-fold structure (Ico structure)	a	250.41414	415.77628
	b	-48.31048	-77.79889
	c	0.12116	0.11552

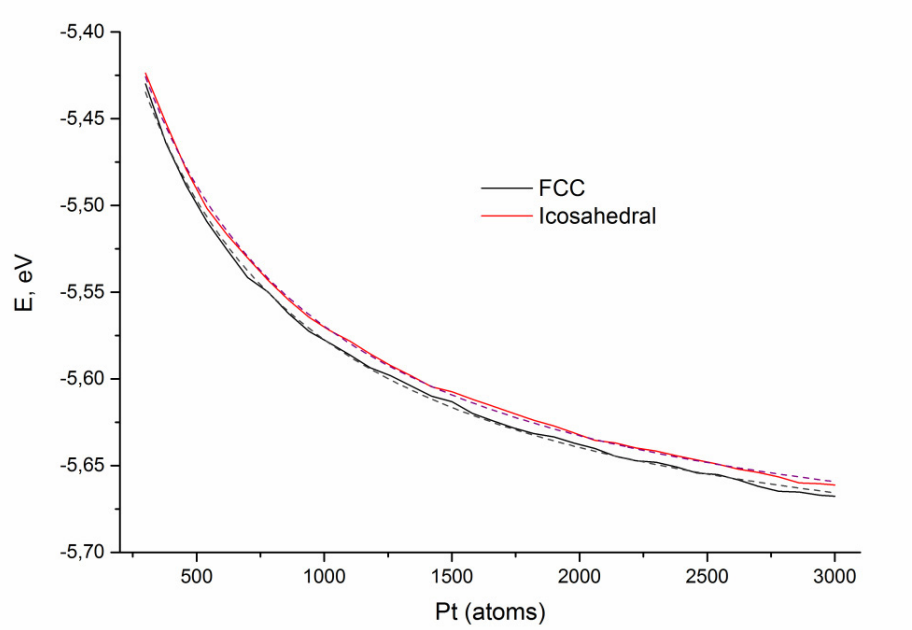

Fig. 3. The mean energy (E) per atom dependency on the size for nanoparticles from the arbitrary number of atoms, the approximation is dotted.

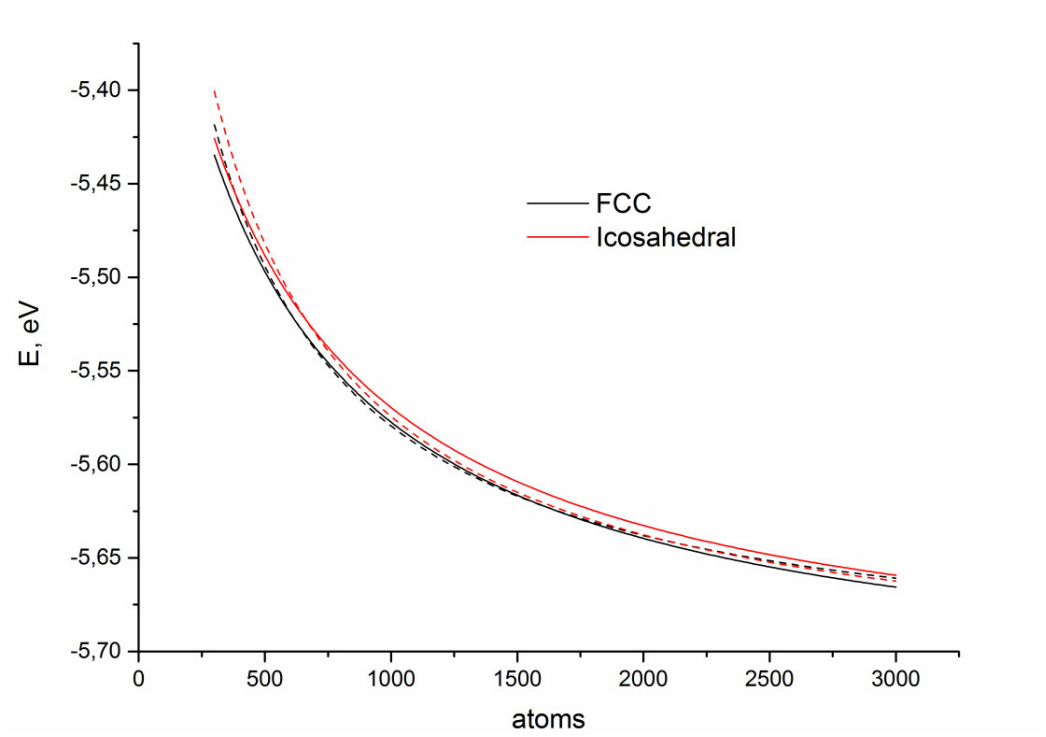

Fig. 4. The approximations comparison, the approximation for the nanoparticles with the number of atoms equal to the magic numbers is dotted.

The analysis of the offered dependences revealed the following theoretical results:

- the ideal shapes for the five-fold symmetry structure are apparently the minimum energy shapes as the lower energy shapes were not found out;
- the shapes with lower energy were found out for the face-centered cubic lattice, that is why the energy dependencies graph on the number of atoms moves down relative to the shapes with magic number of atoms.

Consequently, the results obtained for the arbitrary number of atoms show that for platinum on the studied interval there is no transition from the five-fold symmetry structure to the crystal one because it obviously has less than 300 atoms. Nevertheless the dependency form proposed in the paper [9] coincides with the revealed one in this investigation.

5. Conclusion

The equilibrium shapes of platinum nanoparticles sized from 300 to 3000 atoms with 80 atoms step for the five-fold symmetry lattice and the face-centered cubic one were calculated by the Monte-Carlo method, the dependency of the mean energy of a nanoparticle atom on the atoms amount was offered, such as: $y = c + (a + x)/(b - x / 5.84)$. According to the data of the paper [9] the analogous dependency was offered. The constant -5.84 is equal to the cohesive energy, and the parameter c shows the difference between the asymptote of the offered dependency and cohesive energy. Since it does not exceed 0.12 it is possible to consider the proposed model as a good approximation of atomistic simulation results. In contrast to the offered dependency the logarithmic function does not have an asymptote at $x \to +\infty$ that contradicts the mean atom energy convergence to the cohesive energy for the large sized particles. It was shown that the transition interval from the five-fold symmetry structures to the face-centered cubic ones for platinum is less than 300 atoms and is beyond the scope of the conducted research. Henceforth we plan to continue and extend the calculations for other transitional metals.

Acknowledgements

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References

[1] D.J Wales, Doye, J.P.K., Dullweber, A.: Cambridge Cluster Database (2012). http://www-wales.ch.cam.ac.uk/CCD.html. Accessed 30 Apr 2012

[2] W. Huang, Lai, X., Xu, R.: Structural optimization of silver clusters from to using a Modified Dynamic Lattice Searching method with Constructed core. Chem. Phys. Lett. 507(1–3), 199–202 (2011).

[3] R. Ferrando, Rossi, G., Nita, F., Barcaro, G., Fortunelli, A.: Interface-stabilized phases of metal-on-oxide nanodots. ACS Nano 2(9), 1849–1856 (2008).

[4] R. Ferrando, Rossi, G., Levi, A.C., Kuntovar, Z., Nita, F., Jelea, A., Mottet, C., Barcaro, G., Fortunelli, A., Goniakowski, J.: Structures of metal nanoparticles adsorbed on MgO(001). I. Ag and Au. J. Chem. Phys. 130(17), 174702-1–174702-9 (2009).

[5] S. Ino,: Stability of multiply-twinned particles. J. Phys. Soc. Jpn. 27, 941–953 (1969).

[6] B. Wang, Liu, M., Wang, Y., Chen, X.: Structures and energetics of silver and gold nanoparticles. J. Phys. Chem. C 115(23), 11374–11381 (2011).

[7] C. Barreteau, Desjonque`res, M.C., Spanjaard, D.: Theoretical study of the icosahedral to cuboctahedral structural transition in Rh and Pd clusters. Eur. Phys. J. D 11(3), 395–402 (2000).

[8] F. Baletto,Ferrando, R., Fortunelli, A., Montalenti, F., Mottet, C.: Crossover among structural motifs in transition and noble-metal clusters. J. Chem. Phys. 116(9), 3856–3863 (2002a).

[9] A.V. Myshlavtsev, Stishenko P.V. Relative stability of icosahedral and cuboctahedral metallic nanoparticles // Adsorption. 2013, Vol. 19, Iss. 2-4, pp. 795-801.

[10] A.P. Sutton, Chen J. Long-range Finnis-Sinclair potentials // Philosophical Magazine Letters. 1990, Vol.61, No.3, pp. 139 – 146.

[11] Y. Kimura, Qi, Y., Cëa˘gi, T., Goddard III, W.A.: The quantum Sutton–Chen many-body potential for properties of fcc metals. Technical Report, California Institute of Technology (1998)

[12] A.V. Myshlyavcev Modifikaciya algoritma Metropolisa dlya modelirovaniya metallicheskikh nanochastic для [Tekst] / A.V. Myshlyavcev, P.V. Stishenko // Omskii nauchnyi vestnik. Ser. Pribory, mashiny i tehnologii, 2012, № 1 (107), S. 21-25. Bibliogr.: 14 nazv. (In Russian)